

(19) Japanese Patent Office (JP)

(11) Unexamined Patent  
Application No:

(12) Unexamined Patent Gazette (A)

Kokai 5-213816

(43) Date of Publication August 24, 1993

(51) Int. Cl. <sup>5</sup>	Class. Symbols	Internal Office Registration Nos.:	FI	Technical Classification Field
C 07 C 63/26	E	8930-4H		
51/265				
// B 01 J 31/04				
C 07 B 61/00	300			
Request for Examination: Not yet submitted		Number of Claims: 2		(Total of 4 pages [in the original] )
(21) Application No.:	4-21280	(71) Applicant:	000005968 Mitsubishi Chemical Corporation 2-5-2 Marunouchi, Chiyoda-ku, Tokyo	
(22) Date of Filing:	February 6, 1992	(72) Inventor:	Hideo Takada c/o Mitsubishi Chemical Corporation, Kurosaki Plant; 1-1 Kurosakishiroishi, Kitakyushu-shi, Fukuoka-ken	
		(72) Inventor:	Shotoku Nishio c/o Mitsubishi Chemical Corporation, Matsuyama Plant; 3-580 Ookaga, Matsuyama-shi, Ehime-ken	
		(74) Agent:	Takeshi Shigeno, Patent Attorney	

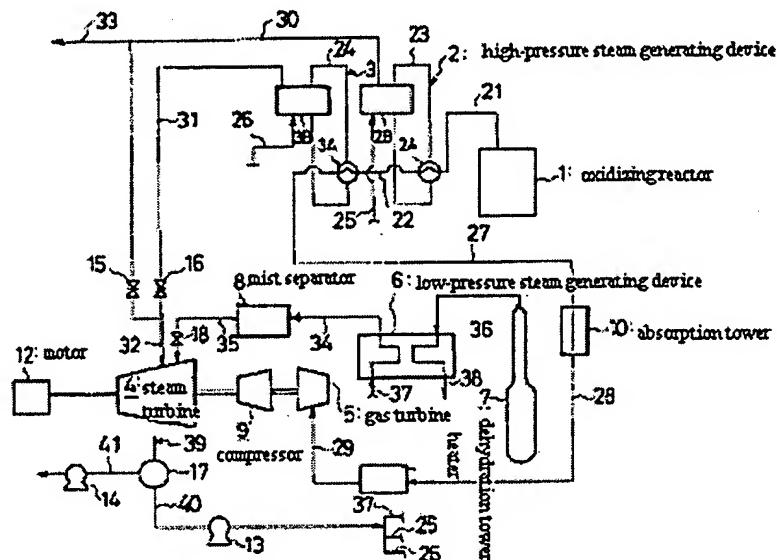
(54) [Title of the Invention] Method For Manufacturing Aromatic Carboxylic Acid

(57) [Summary]

[Object] To effectively utilize the waste heat resulting from the process of oxidizing an alkyl aromatic hydrocarbon to manufacture an aromatic carboxylic acid, to improve energy efficiency, and to reduce energy costs.

[Means of Achievement] Exhaust gas from an oxidation reactor 1 is fed to a gas turbine 5 after passing through high-pressure steam generating devices 2 and 3. The high-pressure steam generated from the high-pressure steam generating devices 2 and 3 is fed to a steam turbine 4. A compressor 9 for feeding compressed air to the reactor is operated by the power output obtained by operating the gas turbine 5 and the steam turbine 4.

**[Merits]** The steam turbine and the gas turbine are operated by the waste heat from the manufacturing process of an aromatic carboxylic acid, and the power output thereof can be effectively utilized as a power source for the air compressor.



## [Claims]

[Claim 1] A method for manufacturing an aromatic carboxylic acid in an oxidation reactor by oxidizing an alkyl aromatic hydrocarbon with gas containing molecular oxygen in a lower aliphatic carboxylic acid solvent, wherein the method for manufacturing an aromatic carboxylic acid is characterized in that exhaust gas from an oxidation reactor is fed to a gas turbine after passing through high-pressure steam generators, the high-pressure steam generated from the high-pressure steam generators is fed to a steam turbine, an air compressor is operated by the power output obtained by operating the gas turbine and the steam turbine, and the compressed air from the air compressor is used as the gas containing molecular oxygen.

[Claim 2] A method for manufacturing an aromatic carboxylic acid, characterized in that in the method according to claim 1, the aromatic carboxylic acid is removed from the solution produced by the oxidizing reaction; then, as the lower aliphatic carboxylic acid solvent is recovered from the dehydrating tower, the steam that is removed from the dehydrating tower is passed through a low-pressure steam generator and expelled to the exterior; and the low pressure

steam generated from the low-pressure steam generator is fed to the steam turbine together with the high-pressure steam.

### **[Detailed Description of the Invention]**

**[0001]**

**[Technological Field of the Invention]** The present invention relates to a method for manufacturing an aromatic carboxylic acid by oxidizing an alkyl aromatic hydrocarbon, and particularly relates to a method for effectively utilizing the waste heat from a manufacturing process, improving energy efficiency, and reducing energy costs.

**[0002]**

**[Prior Art]** In conventional practice, methods are well known for manufacturing an aromatic carboxylic acid, for example terephthalic acid, in an oxidation reactor by oxidizing an alkyl aromatic hydrocarbon, for example paraxylene, with gas containing molecular oxygen in a lower aliphatic carboxylic acid solvent.

**[0003]** In this method, the high-temperature, high-pressure reactant exhaust gas expelled from the oxidation reactor contains large quantities of solvent steam and water vapor. The lower aliphatic carboxylic acid used as a reaction solvent is normally recovered by distillation after the product is separated, but large quantities of gas at normal pressure are also discharged from the dehydrating tower for distillation recovery.

**[0004]** In conventional practice, the reactant exhaust gas expelled from the oxidation reactor passes through the steam generator and functions as a heat source for steam generation, then passes through a condenser and an absorption tower, and is either discharged into the atmosphere or is utilized as motive energy for a gas turbine or the like.

**[0005]** Other methods are known (Japanese Patent Application Laid-open No. S56-40636) in which the reactant exhaust gas is fed directly to a gas turbine or the like for heat waste utilization in order to more effectively utilize the waste heat from the reactant exhaust gas.

**[0006]**

**[Problems Which the Invention Is Intended to Solve]** In methods commonly used in conventional practice, wherein the reactant exhaust gas is fed to the steam generator and steam is generated, the steam generated by the steam generator is normally dispersed and fed to each

location in the plant requiring steam, and the excess is discharged into the atmosphere, which is not necessarily sufficient with respect to effective utilization of steam.

[0007] When the method described in Japanese Patent Application Laid-open No. S56-40636 is put to actual use, all the devices must be made of titanium or another such corrosion resistant material, which in reality is not suitable for recovering stable waste heat over a long period of time.

[0008] In order to solve the problems in conventional practice described above, an object of the present invention is to provide a method for manufacturing an aromatic carboxylic acid intended to more effectively utilize the waste heat resulting from the process of oxidizing an alkyl aromatic hydrocarbon to manufacture an aromatic carboxylic acid, to improve energy efficiency, and to reduce energy costs.

[0009]

**[Means Used to Solve the Above-Mentioned Problems]** The method for manufacturing an aromatic carboxylic acid according to claim 1 entails manufacturing an aromatic carboxylic acid in an oxidation reactor by oxidizing an alkyl aromatic hydrocarbon with gas containing molecular oxygen in a lower aliphatic carboxylic acid solvent, wherein this method is characterized in that exhaust gas from an oxidation reactor is fed to a gas turbine after passing through high-pressure steam generators, the high-pressure steam generated from the high-pressure steam generators is fed to a steam turbine, an air compressor is operated by the power output obtained by operating the gas turbine and the steam turbine, and the compressed air from the air compressor is used as the gas containing molecular oxygen.

[0010] The method for manufacturing an aromatic carboxylic acid according to claim 2 is characterized in that in the method according to claim 1, the aromatic carboxylic acid is removed from the solution produced by the oxidizing reaction; then, as the lower aliphatic carboxylic acid solvent is recovered from the dehydrating tower, the steam that is removed from the dehydrating tower is passed through a low-pressure steam generator and expelled to the exterior; and the low pressure steam generated from the low-pressure steam generator is fed to the steam turbine together with the high-pressure steam.

[0011] In the present invention, the term "high-pressure steam" indicates steam with a pressure far greater than normal, for example 1.5 atm or greater; the term "low-pressure steam" indicates

steam with a pressure far less than normal, for example 0.9 atm or less; and the term "steam at normal pressure" indicates steam at 1-1.2 atm.

[0012] Terephthalic acid, isophthalic acid, phthalic acid, *p*-toluic acid, naphthalene dicarboxylic acid, and the like are examples of the aromatic carboxylic acid manufactured in the present invention, and the alkyl aromatic hydrocarbons corresponding to each of these are used as a starting material.

[0013] Acetic acid, propionic acid, and the like are given as examples of the lower aliphatic carboxylic acid used as a solvent, but normally acetic acid is used.

[0014] In order to manufacture terephthalic acid according to the method for manufacturing an aromatic carboxylic acid of the present invention, paraxylene, for example, is subjected to liquid-phase oxidation in an acetic acid solvent by molecular oxygen in the presence of a catalyst comprising cobalt acetate, manganese acetate, and a bromine compound. Hydrogen bromide, sodium bromide, and the like may be given as examples of the bromine compound used herein. For the added amount of the catalyst, cobalt acetate and manganese acetate are normally 100-1000 ppm as each metallic content in relation to the solvent, and the bromine compound is normally 300-3000 ppm as the bromine content in relation to the solvent.

[0015] Normally 1-10 parts by weight of the solvent acetic acid is used per 1 part by weight of paraxylene. The acetic acid may also contain about 30% by weight of water. The reaction is normally conducted at a temperature of 150-230°C and at a pressure of 2-100 atm, and air is normally used as the gas containing molecular oxygen.

[0016] The terephthalic acid generated by the oxidation reaction is normally separated from the liquid products of the oxidation reaction by crystallization, centrifugation, or the like. Since the main component of the mother liquor of the reaction after the terephthalic acid is separated is acetic acid, part of the mother liquor of the reaction can be returned as is to the reaction system, but normally the acetic acid solvent and the water content are separated by evaporation in which either a large part or all of the mother liquor is boiled up. The boiled aqueous acetic acid is used again after some of the water content is removed in a distillation dehydration tower.

[0017]

**[Operation of the Invention]** According to the method for manufacturing an aromatic carboxylic acid in claim 1, a steam turbine and a gas turbine are operated by the waste heat from

the process of manufacturing the aromatic carboxylic acid, and the power output thereof can be effectively utilized as the power source for an air compressor.

[0018] According to the method for manufacturing an aromatic carboxylic acid in claim 2, the heat energy of most of the steam expelled from the dehydration tower for recovering the lower aliphatic carboxylic acid solvent can also be effectively utilized.

[0019]

[Practical Examples] A practical example of the present invention is described in detail below with reference to the diagram.

[0020] Fig. 1 is a block diagram showing one example of a terephthalic acid manufacturing apparatus suitable for implementing the present invention.

[0021] The apparatus of the present embodiment has two high-pressure steam generating devices 2 and 3 downstream of an oxidizing reactor 1, and the high-pressure steam generating devices 2 and 3 comprise heat exchangers 2A and 3A and steam generators 2B and 3B. The symbol 4 denotes a steam turbine, 5 is a gas turbine, 6 is a low-pressure steam generating device, 7 is a dehydration tower, 8 is a mist separator, 9 is a compressor, 10 is an absorption tower, 11 is a heater, 12 is a motor, 13 is a condensed water pump, 14 is a vacuum pump, 15 and 16 are pressure regulators, 17 is a heat exchanger, and 18 is a valve. The symbols 21-41 indicate pipes.

[0022] In the present embodiment, the exhaust gas expelled from the oxidation reactor is fed to the heat exchanger 2A of the high-pressure steam generating device 2 through the pipe 21 and then to the heat exchanger 3A of the high-pressure steam generating device 3 through the pipe 22, heat is absorbed by the water circulation through the pipes 23 and 24, and high-pressure steam is generated from the steam generators 2B and 3B.

[0023] The condensed water produced from the exhaust steam of the steam turbine 4 (to be described later) through the heat exchanger 17 is fed as make-up water to the steam generators 2B and 3B through the pipes 25 and 26.

[0024] The exhaust gas from the heat exchanger 3A is fed through the pipe 27 to the absorption tower 10, where the solvent (acetic acid) components contained in the absorption tower 10 are removed by absorption. The gas in the absorption tower 10, in which the acetic acid content is several hundred parts per million or less, is fed through the pipe 28 to the heater 11, preheated in the heater 11, and fed through the pipe 29 to the gas turbine 5.

[0025] The steam generated by the steam generators 2B and 3B is fed through the pipes 30, 31, and 32 to the steam turbine 4. The system is designed such that the pipe 33 branches off from the pipe 30, about 90% of the high-pressure steam generated by the high-pressure steam generating device 2 (normally about 6 atm) is fed to another system in the manufacturing plant requiring steam, and the remaining 10% of the high-pressure steam is fed to the steam turbine 4. Meanwhile, all of the high-pressure steam generated by the high-pressure steam generating device 3 (normally about 1.5 atm) is fed to the steam turbine 4. The pipe 30 and the pipe 31 are provided with the pressure regulators 15 and 16, respectively; and the high-pressure steam, regulated to a specific pressure, is fed to the steam turbine 4.

[0026] The low-pressure steam generated by the low-pressure steam generating device 6 (normally about 0.7 atm) to be described later is also fed to the steam turbine 4 through the pipe 35, which comprises the pipe 34, mist separator 8, and valve 18.

[0027] The steam at substantially normal pressure (commonly about 1.1 atm), generated by the dehydration tower 7 for recovering the acetic acid from the mother liquor in which the acetic acid is a primary component after removal of the terephthalic acid produced from the liquid reaction product in the oxidizing reactor 1, is fed through the pipe 36 to the low-pressure steam generating device 6, where heat is exchanged with the make-up water fed from the pipe 37, and low-pressure steam is generated. As described above, the generated low-pressure steam is fed from the pipe 34 through the mist separator 8 and the pipe 35 to the steam turbine 4. The condensed water is expelled outside of the system through the pipe 38.

[0028] The exhaust steam from the steam turbine 4 is fed to the heat exchanger 17 through the pipe 39, and the condensed water produced by the heat exchanger 17 is passed through the pipe 40 provided with the condensed water pump 13, and is circulated through the pipes 25 and 26 as make-up water for the steam generators 2B and 3B described above, and also through the pipe 37 as make-up water for the low-pressure steam generating device 6 described above. The uncondensed gas from the heat exchanger 17 is expelled outside of the system through the pipe 41 and the vacuum pump 14.

[0029] Thus, in the method of the present invention, the steam turbine 4 operated by inputting the energy from both the high-pressure steam and the low-pressure steam, and the gas turbine 5 operated by inputting the energy from the exhaust gas of the high-pressure steam generating device are connected directly to the compressor 9 for obtaining compressed air that is fed as a

source of oxygen to the oxidizing reactor 1, and the steam turbine 4 and the gas turbine 9 function as a source of power for the compressor 9.

[0030] Normally, the power outputs of the steam turbine 4 and the gas turbine 5 are approximately equal at about 47% of the required energy for the compressor 9.

[0031] Consequently, the power outputs of the steam turbine 4 and the gas turbine 5 alone are insufficient for the energy required to operate the compressor 9, therefore the motor 12 is added as necessary in the manner shown in Fig. 1 to compensate for the lacking energy (about 6% ( $= 100 - 47 \times 2$ )).

[0032] The method shown in Fig. 1 is one practical method of the present invention, and the present invention need not be limited to the practical example shown in the diagram so long as it does not deter from the purpose thereof, and various other embodiments can be employed, such as embodiments for the installation of each device. For example, the number of high-pressure steam generating devices installed need not be limited to two, and there can be more than one or even three or more reactors and dehydration towers if they comply with the conditions for size and configuration.

[0033] Increasing the proportion in which the high-pressure steam generated by the high-pressure steam generating device 2 is fed to the steam turbine 4 makes it possible to raise the power output of the steam turbine 4 and to cease operating the motor 12.

[0034]

**[Merits of the Invention]** As described in detail above, according to the method for manufacturing an aromatic carboxylic acid of the present invention, as an alkyl aromatic hydrocarbon is oxidized to manufacture an aromatic carboxylic acid, the waste heat generated by the manufacturing process can be very effectively utilized, the energy ratio can be improved, and energy costs can be reduced.

[0035] According to the method in claim 2, more efficient utilization of waste heat is made possible.

**[Brief Description of the Drawings]**

**[Figure 1]** A block diagram showing one example of a terephthalic acid manufacturing apparatus suitable for implementing the present invention.

**[Key]**

- 1: oxidizing reactor
- 2, 3: high-pressure steam generating device
- 4: steam turbine
- 5: gas turbine
- 6: low-pressure steam generating device
- 7: dehydration tower
- 8: mist separator
- 9: compressor
- 10: absorption tower
- 11: heater
- 12: motor
- 13: condensed water pump
- 14: vacuum pump
- 15, 16: pressure regulator
- 17: heat exchanger
- 18: valve

[Fig. 1]

